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Preliminary communication

ASYMMETRIC INDUCTION IN THE COURSE OF INTERNAL PALLADATION OF ENANTIOMERIC 1-DIMETHYLAMINOETHYLFERROCENE

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Summary

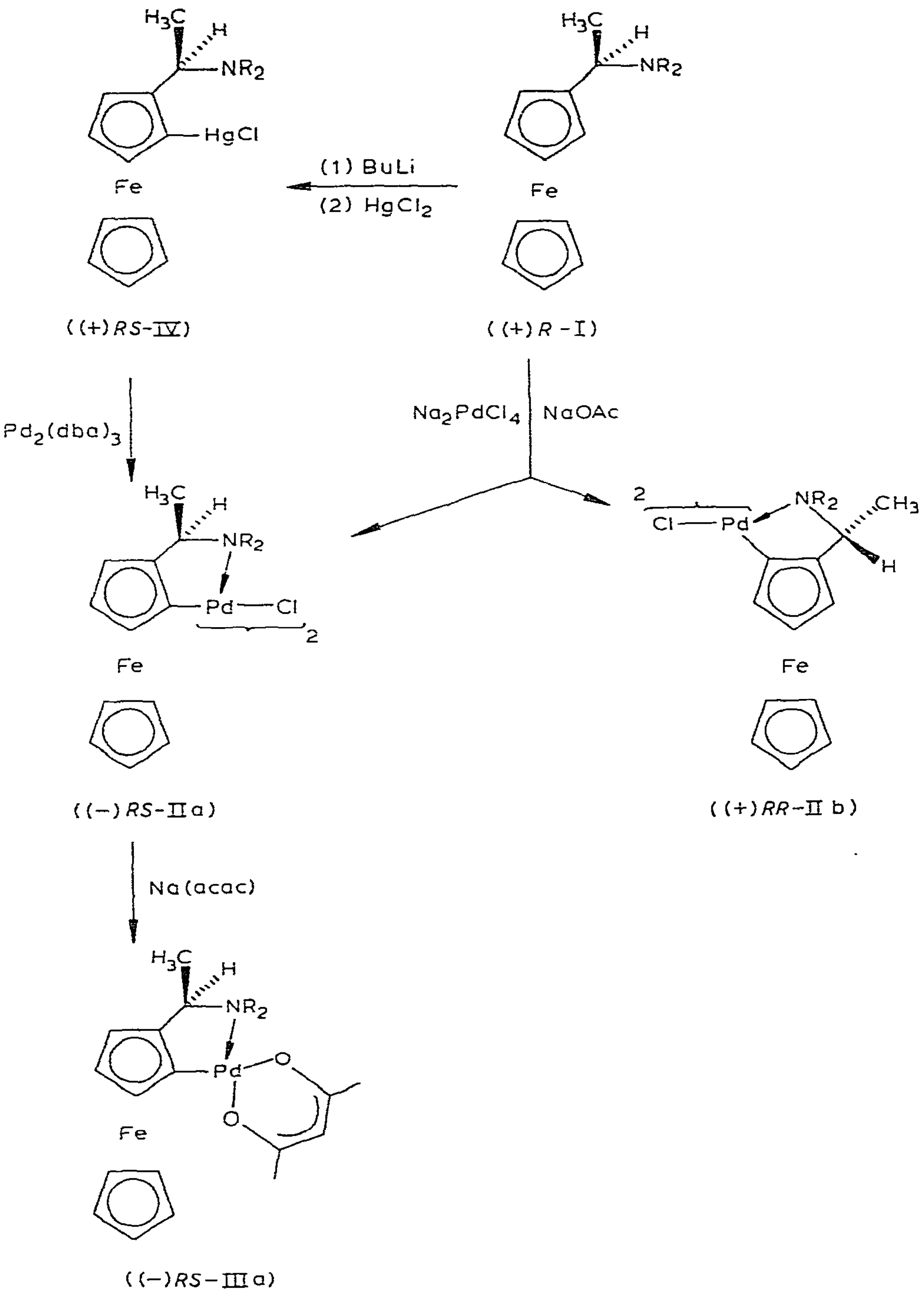
The internal palladation of optically active 1-dimethylaminoethylferrocene proceeds with stereoselectivity 85/15, that is less stereoselective than the asymmetrically induced lithiation of this amine, the sense of diastereomeric preference being the same.

During the course of work directed at developing new synthetic routes to platinum(II) and palladium(II) complexes [1, 2], we have prepared dimeric 2-chloropalladio-1-dimethylaminomethylferrocene containing a plane of chirality, and have resolved it into enantiomers [3]. In this communication we report the sequence of reactions shown in Scheme 1 which allows us to evaluate the degree of asymmetric induction in the course of the direct palladation of optically active 1-dimethylaminoethylferrocene (I).

Both enantiomers of I, $[\alpha]_D^{20}$ ± 14.4° (*c* 2.7, ethanol) were obtained by Ugi's method [4]. The palladation of (+)-I with Na_2PdCl_4 in MeOH in the presence of sodium acetate [5] produces in 84% yield a mixture ($[\alpha]_D^{20}$ −316°, *c* 0.39, CH_2Cl_2) of two diastereoisomers (−)-IIa and (+)-IIb in which (−)-IIa prevails. Dimers of (−)-IIa and (+)-IIb having the same absolute configuration at the chiral centre and opposite absolute configuration of the chiral plane were first separated by hand picking of single crystals and further recrystallized from benzene/hexane. The optically pure (−)-IIa ($[\alpha]_D^{20}$ −472.7°, *c* 0.44, CH_2Cl_2) and (+)-IIb ($[\alpha]_D^{20}$ +475.4°, *c* 0.39, CH_2Cl_2) were obtained and identified by elemental analysis and NMR spectra.

On the other hand, metalation of (+)-I with n-butyllithium proceeded with stereoselectivity 96/4 [6] and subsequent treatment with mercuric chloride led to the mercurial (+)-IV. Recrystallization from methanol afforded optically pure (+)-IV ($[\alpha]_D^{20}$ +34.4°, *c* 4.0, CH_2Cl_2).

Reaction of (+)-IV with $Pd_2DBA_3 \cdot C_6H_6$ evidently proceeds with complete configurational retention to give optically pure (−)-IIa ($[\alpha]_D^{20}$ −478.6°, *c* 0.4, CH_2Cl_2).



The value of optical rotation has been measured for a mixture of the optically active dimers IIa+IIb taken directly from palladation of (+)-I or (−)-I. Hence the stereoselectivity of this reaction has been found by comparison with an optically pure sample of (−)-IIa. In order to exclude the plausible effect of a dimeric bridged structure on optical rotation (−)-IIa and (−)-IIa+IIb were transformed by treatment with sodium acetylacetonate into (−)-IIIa and (−)-IIIa+IIIb. However, the optical rotations observed for (−)-IIa and (−)-IIIa were almost identical, and this indicates additivity upon dimer formation. The degree of asymmetric induction calculated independently from experiments with (+)- or (−)-I appeared to be a diastereoisomeric excess of 70±2% or a diastereoisomer ratio of 85/15. Hence the metalation of I with a transition metal (palladium) salt proceeds with noticeably lower stereoselectivity while the lithiation with n-butyllithium [6] exhibits 92%. This decrease is likely to be related to the difference in mechanisms of these two metalation reactions.

From Ugi's work [7] one may assign *RS*-configuration to (+)-IV and (−)-IIa (the major product of the direct palladation of (+)-I), and *RR*-configuration to the minor product (+)-IIb.

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